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The Raman Spectra of some Inorganic Chlorides

By

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Abstract

The paper gives the results of a study of the Raman spectra of thionyl chloride, sulphur monochloride, phosphorus trichloride, phosphorus oxychloride and boron trichloride. The Raman frequencies of thionyl chloride are identified with the various modes of oscillation of this system discussed by Mecke. A special feature of the spectrum of this liquid is the unusually large intensity of the lines arising from the transverse oscillations. The frequency of oscillation of the SO group is not appreciably affected by differences in the valency of the sulphur atom. The structure of S_2Cl_2 molecule is discussed and evidence from the Raman spectra shows that it should be represented by the formula Cl—S—S—Cl. The spectrum of $POCl_3$ gives a line at $\triangle\nu 1290$ which is identified with the PO linkage. A large difference is noticed in the relative intensities of the lines at $\triangle\nu 388$ in PCl_3 and $POCl_3$. The spectrum of boron trichloride shows similarity to the spectra of the other trichlorides, but a reversal in the relative order of intensities of the lines is observed. This may be connected with the low atomic weight of this element.

1. *Inrtoduction.*

Investigations on the Raman spectra of some inorganic chlorides were carried out by the author sometime ago and the results are reported in this paper. The experimental arrangements described in the earlier papers were adopted.

Kahlbaum's liquids were used after distillation in vacuo. A Fuess glass spectrograph of large dispersion (49 mm. between λ3984 and λ4916) was used and iron arc comparison spectrum was taken in every case.

2. *Results.*

Thionyl chloride : —The liquid shows strong Raman lines and becomes slightly yellow on exposure to mercury light. The results are given in the following table.

TABLE I.

Thionyl chloride.

Raman lines		Exciting line λ	$\Delta\nu$	Raman lines		Exciting line λ	$\Delta\nu$
Intensity	ν (vac)			Intensity	ν (vac)		
1	23282	4358·3	−344	10	21707	4358·3	1231
1	23220	,,	−282	1	18650	5460·7	−342
1	23131	,,	−193	1	18590	,,	−282
8	22744	,,	194	1	18503	,,	−195
8	22656	,,	282	4	18114	,,	194
10	22595	,,	343	4	18026	,,	282
8d	22493	,,	445	6	17965	,,	343
8d	22448	,,	490	3d	17864	,,	444
				3d	17819	,,	489

$\Delta\nu$:—	194,	282	343	445	489	1231
	(8)	(8)	(10)	(8d)	(8d)	(10)
μ	51·5	35·5	29·2	22·47	20·45	8·12

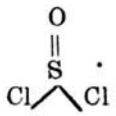
The compound gives six Raman frequencies of which the one at $\Delta\nu$1231 is the most intense. $\Delta\nu$445 and 489 are somewhat diffuse. The values are in excellent agreement with those published recently by Nisi [1] and Matossi and

[1] H. Nisi, Jap. Journ. Phys., VI, Nos. 1, 2 (1930)

Aderhold.[2] The frequency shift 1231 is present in all compounds containing SO linkage and does not appear to be influenced markedly by the changes in the valency of the sulphur atom. This interesting feature is brought out from the data collected below.

TABLE II.

Substance	Author	$\Delta\nu$	Substance	Author	$\Delta\nu$	Substance	Author	$\Delta\nu$
SO_2	S.B[3]	1146	H_2SO_4	G&V[5]	1149	$R.SO_3H$	H. N[6]	1128
SO_3	,,	1068	$SO_2(OH)(Cl)$	H. N[6]	1155	RSO_2Cl	,,	1168
SO_4 (ion)	C.R[4]	1102	SO_2Cl_2	,,	1192	$SO(OC_2H_5)_2$	,,	1209
(Sulphate solutions)						$SOCl_2$	S. V.[7]	1231

The constitution of thionyl chloride is represented by the formula  . On theoretical considerations a system of this type may be expected to give six frequencies and all of them are obtained with the liquid. According to Mecke three modes of vibrations are possible for such a system, *viz.*, (1) one in which the sulphur atom remains fixed and the chlorine and oxygen atoms vibrate symmetrically along the chemical bonds, (2) where the two chlorine atoms remain fixed and oxygen and sulphur atoms vibrate against each other, and (3) where the SO group moves as a whole along

[2] F. Matossi and H. Aderhold Z. f. Phys. 68, 689 (1931)
[3] S. Bhagavantam. Ind. Journ. Phys., V, 59 (1930)
[4] C. Ramaswamy, Ind. Journ. Phy., V, 193 (1930)
[5] A. S. Ganesan and S. Venkateswaran. Ind. Journ. Phy., IV, 195 (1930)
[6] H. Nisi. loc. cit.
[7] S. Venkateswaran, this paper.

the chemical bonds while the two chlorine atoms also do the same. Following Matossi and Aderhold[8] we may ascribe the Raman frequencies $\Delta\nu$ 488, 1229 and 192 as arising from the first, second and third type of oscillations respectively, mentioned above. The other frequencies represent displacements transverse to the chemical bonds. It should be noted that the lines due to these transverse oscillations are very intense in thionyl chloride. This feature is of great interest, in view of the fact that transverse vibrations do not usually appear in the Raman spectra, and if they appear at all, they do so, only very weakly.

As the constitution of phosgene is analogous to that of thionyl chloride a comparison of their spectra may be made here. Dadieu and Kohlrausch[9] have investigated the Raman spectrum of phosgene and their values are given below.

TABLE III.

Substance	$\Delta\nu$					
$O=S\begin{matrix}Cl\\Cl\end{matrix}$	194	282	343	445	489	1231
$O=C\begin{matrix}Cl\\Cl\end{matrix}$		301	444	571	834	1810

The frequency 282 of thionyl chloride corresponds to 301 of phosgene. It is remarkable that the value of this frequency remains identical in the two compounds in spite of the differences in their chemical nature.

[8] *loc. cit.*

[9] Wien. Ber. 139, 717 (1930)
See also Henri and Howell, Proc. Roy. Soc.

Sulphur monochloride :—The liquid had a pure yellow colour, free from any tinge of red indicating that it was not contaminated with the higher chlorides. Table IV gives the analysis of its Raman spectrum. The values obtained by Nisi[10] and Matossi and Aderhold[11] are also given for comparison.

TABLE IV.

Sulphur monochloride.

Raman lines.		Exciting line λ	Δν	Raman lines.		Exciting line λ	Δν
Intensity	ν(vac.)			Intensity	ν(vac.)		
4d	18201	5460·7	107	6dv	17859	5460·7	449
2	18098	,,	210	0	17763	,,	545
0	18060	,,	248				

Δν :—107,	210,	248,	449,	545
(4d)	(2)	(0)	(6d)	(0)
μ :—93·5	47·6	40·3	22·3	18·3
Nisi Δν :—103	213		446	
*Matossi ,, 110 and Aderhold	200	249	451	

The liquid gives five frequencies of which Δν 449 is the most intense. The corresponding Raman line is distinctly diffuse towards the violet side. The frequency at 107 comes next in order of intensity and is also diffuse. Those at 248 and 545 are very weak, the latter being reported for the first time.

Molecular weight determinations show that the formula of sulphur monochloride is S_2Cl_2. Two constitutional formulæ have been proposed, one where each of the sulphur atom has a chlorine atom attached to it, and the other in which both the chlorine atoms are bound to the same sulphur atom. According to Michaelis and Schifferdecker,[12] Thorpe and others[13]

[10] *loc. cit.*

[11] *loc. cit.*

[12] A. Michaelis and O. Schifferdecker, Ber., 6, 993, (1873)

[13] T. E. Thorpe, Journ. Chem. Soc., 37, 141, 327, (1880)

the structure of the molecule is represented by $S=S\langle^{Cl}_{Cl}$, analogous with thionyl chloride $O=S\langle^{Cl}_{Cl}$. On the other hand, Holmberg,[14] Bruni and Amodori [15] and others favour the formula Cl – S – S – Cl, analogous with hydrogen disulphide H – S – S – H. From the heat of formation of S_2Cl_2 Thomlinson [16] found that the theoretical and experimental values agree best on the assumption that the contained sulphur is bivalent. Chemical evidence is, therefore, not decisive in respect of the constitution of this compound.

A study of the Raman spectrum of the liquid throws new light on this question. The existence of five frequencies shows that the molecule cannot be diatomic (SCl) and supports the formula S_2Cl_2. Two questions arise for solution in this connection, namely, (1) whether the two chlorine atoms are attached to the same or different sulphur atoms, and (2) whether the two sulphur atoms are attached by a single or double bond. If the two chlorine atoms are attached to the same sulphur atom in S_2Cl_2 the structure should be similar to that of $SOCl_2$ and $COCl_2$. A comparison of the spectra of the three compounds, however, shows that the frequency shift 282 which is prominent in both $SOCl_2$ and $COCl_2$ fails to appear in S_2Cl_2 in striking contrast to the other two compounds. This frequency represents an oscillation in which the chlorine atoms take the largest share. $\Delta\nu$ 285 is, again absent in methyl chloride ($\gtrless C-Cl$) where only one chlorine atom is attached to the Carbon atom but appears strongly in methylene chloride $\left(\rangle C\langle^{Cl}_{Cl}\right)$ where the two clorine atoms are attached to the same carbon atom. Further, comparing the spectra of thionyl chloride and phosgene we find that the maximum frequency shift in each case, *viz.*, 1231 in $SOCl_2$

[14] B. Holmberg, Liebig's Ann., *359*, 81, (1908)
[15] G. Bruni and M. Amodori, Atti, Accad, Lincei, *28*, 217, (1919)
[16] J. C. Thomlinson, Chem. News., *95*, 145 (1907)

and 1810 in $COCl_2$ which are both prominent arise respectively from SO and PO groups. On this view, if S_2Cl_2 has a similar structure, the most prominent frequency 449 which should be attributed to the SS group should likewise be the maximum.* The presence of a higher frequency at 545 in this compound is definitely againt such a view. The above results suggest that the two chlorine atoms are presumably *not* bound to the same sulphur atom, and that its structure is different from that of $SOCl_2$ or $COCl_2$.

We may now consider the nature of the binding between the two sulphur atoms in S_2Cl_2. In the investigation on the Raman spectra of some organic sulphides and disulphides [17] it was shown that the S—S bond gives a characteristic frequency 512, while the frequency of vibration of S_2 (S=S) as obtained by fluorescence and absorption of sulphur vapour is $\nu=724{\cdot}5$. The values of these two frequencies, (512 for S—S and 724·5 for S=S) are exactly in the ratio 1 : $\sqrt{2}$ as should be expected. In S_2Cl_2 the frequency 449 is the strongest and is evidently connected with the SS oscillation. This low value suggests that the bond attaching the two sulphur atoms is single (S—S) and not double (S=S) as put forward by Matossi and Aderhold. [18] The result points to the fact that in analogy with methyl and ethyl disulphides the two sulphur atoms in sulphur monochloride are bound by a single bond. Since it has also been shown (see previous paragraph) that each of the two chlorine atoms is attached to a different sulphur atom in the S_2Cl_2 molecule we are led to the conclusion that both the sulphur atoms are bivalent and that the structural formula should be represented by Cl—S—S—Cl. The view held by Matossi and Aderhold that S_2Cl_2 should be represented by the formula $S=S\langle^{Cl}_{Cl}$ is not, therefore, in agreement with the above evidence.

* *Cf.* Raman spectra of $CHCl_3$ and $CHBr_3$

17 S. Venkateswaran, Ind. Journ. Phys., VI, 51, (1931)

18 *loc. cit.*

Phosphorus trichloride and oxychloride:—Tables V and VI give the results of the Raman spectra of the two compounds. There was a strong continuous background in the spectrum of phosphorus oxychloride.

TABLE V.

Phosphorus trichloride.

Raman lines.		Exciting line λ	Δν	Raman lines.		Exciting line λ	Δν
Intensity.	ν (vac).			Intensity	ν (vac)		
2d	25220	4046·6	−515	4	23128	4358·3	−190
2d	25186	,,	−481	1	22805	4347·5	190
3	24963	,,	−258	0	22781	4339·2	258
4	24893	,,	−188	10	22749	4358·3	189
8	24445	,,	260	10	22678	,,	260
1	24256	4077·7	260	1	22605	,,	333
5d	24224	4046·6	481	6d	22456	,,	478
8d	24190	,,	515	10d	22424	,,	514
1d	24035	4077·7	481	3	18119	5460·7	189
2d	24003	,,	513	2	18049	,,	259
2d	23453	4358·3	−515	2d	17825	,,	483
2d	23419	,,	−481	3d	17797	,,	511
3	23197	,,	−259				

Δν	189,	260,	333,	481,	514
	(10)	(10)	(1)	(6d)	(10d)
α	52·9	38·5	30·0	20·8	19·5

TABLE VI.

Phosphorus oxychloride.

Raman lines.		Exciting line λ	Δν	Raman lines.		Exciting line λ	Δν
Intensity.	ν(vac.)			Intensity.	ν(vac.)		
0	24437	4046·6	268	4	22747	4358·3	191
1	24367	,,	338	2	22669	,,	269
3	24219	,,	486	4	22599	,,	339
1 *d*	23415	,,	1290	6	22453	,,	485
0	23276	4358·3	−338	0*d*	22353	,,	585
0	23208	,,	−270	1*d*	21648	,,	1290
2	23129	,,	−191				

Δν :—	191,	269,	338,	485,	585,	1290
	(4)	(2)	(4)	(6)	(0*d*)	(1*d*)
μ :—	52·4	37·2	29·6	20·6	17·1	7·8

The characteristic features of the Raman spectra of the trichlorides have already been pointed out by Daure[19] and by Bhagavantam.[20] With the exception of $\Delta\nu 514$ all the Raman frequencies of phosphorus trichloride are present in the oxychloride also. The line due to the frequency shift 514 is very intense in PCl_3 but is absent in $POCl_3$. A new Raman frequency at 1290 appears in $POCl_3$. This may be attributed to the presence of the P=O group, analogous with the Raman frequency 1231 which is characteristic of the S=O group. (See Table II.)

A striking difference in the relative intensities of the line at $\Delta\nu 338$ is noticed on comparing the spectra of PCl_3 and $POCl_3$. This line appears prominently in the spectra of

19 P. Daure, Compt. Rend., 187, 940 (1928)
20 S. Bhagavantam, Ind. Jour. Phy., V, 85, 73 (1930)

$POCl_3$, while it is just detectable with PCl_3. In view of the fact that this frequency is reported by Daure also, it is not possible to say at present whether its occurrence in PCl_3 is due to the presence of $POCl_3$ as an impurity or whether the large change in the intensities of the corresponding lines in the two liquids is genuine.

Boron trichloride.—The results of the Raman spectrum of this liquid are given in Table VII.

TABLE VII

Boron trichloride.

Raman lines.		Exciting line λ	Δν	Raman lines.		Exciting line λ	Δν
Intensity.	ν(vac.)			Intensity.	ν(vac.)		
1	25176	4046·6	−471	2	23193	4358·3	−255
1	24961	,,	−256	0	22739	4337·5	·256
4	21450	,,	255	6	22683	4358·3	255
0	24261	4077·7	255	0	22523	4347·5	471
10	24233	4046·6	472	10	22467	4358·3	471
1	24044	4077·7	472	0.*d* (double)	21991	,,	947
2	23410	4358·3	−472				

Δν :—	255,	472,	947
	(6)	(10)	(0*d*)
μ :—	39·2	21·2	10·6.

Of the above frequencies Δν 472 is the most intense, Δν255 coming next in order of intensity. The line corresponding to Δν 947 is diffuse and very weak. It shows a doublet structure, but was not properly resolved. Although the spectrum shows certain general features in common with those of the other trichlorides, marked changes in the relative

intensities of some lines are noticed. In the Raman spectra of the trichlorides of phosphorus, arsenic, antimony and bismuth, where the central atom is heavy it is found that the Raman lines corresponding to the longest shifts in frequencies are the most intense. In BCl_3, however, the corresponding lines are the weakest, while the second frequency comes out most prominently. Such a reversal of intensities is presumably connected with the fact that boron is the lightest of the trivalent elements.

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